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CONTRIBUTIONS FROM THE ROGERS LABORATORY OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

LIII. — *ON THE EQUILIBRIUM OF THE SYSTEM CONSISTING OF LIME, CARBON, CALCIUM CARBIDE AND CARBON MONOXIDE.*

By M. DeKay Thompson.

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LIII. — ON THE EQUILIBRIUM OF THE SYSTEM CONSISTING OF LIME, CARBON, CALCIUM CARBIDE AND CARBON MONOXIDE.

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1. Introduction.

While the author of the following paper was working on the subject indicated in the title above, an article dealing with the same matter appeared in the Electrochemical and Metallurgical Industry.[1] The present writer's results did not agree with those in the article referred to, and it was therefore thought best to publish a preliminary paper on the subject, which was accordingly presented at the October meeting of the American Electrochemical Society in New York. As the work has now been brought to a close, the following article will be made complete, including all of the preliminary publication that is necessary for clearness.

According to the Phase Rule[2] the substances taking part in the reaction $CaO + 3C \rightleftarrows CaC_2 + CO$ form a monovariant system, that is to say, for any given temperature there is a definite pressure of carbon monoxide which will preserve equilibrium. In order that equilibrium can exist the reaction must be reversible. The fact that this reaction is reversible has been shown by Rothmund[3] and others.[4] Rothmund also attempted to measure the temperature of formation of carbide by heating to different temperatures lime and carbon, and testing the charge immediately afterwards to see if it reacted with water, giving off acetylene. The furnace used consisted of a carbon tube through

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[1] C. A. Hansen, Electrochem. Met. Ind. 1909, **7**, 427.
[2] See Findlay, "The Phase Rule," p. 16.
[3] Zeitschr. f. anorg. Chem. 1902, **31**, 136.
[4] A. Frank, Zeitschr. f. angew. Chem. 1905, **44**, 1733.

which an electrical current was passed. The assumption that must be made with regard to the partial pressure of the carbon monoxide is that it is constant and is due to oxygen of the air acting on the carbon tube, giving one-third of an atmosphere.[5] Unless the temperature is raised above that corresponding to one-third of an atmosphere, no carbide would be found. By repeated trials this temperature could be located within certain limits, if the above assumption is true. In this way Rothmund found 1620° C. as the temperature of formation. Similar experiments were repeated later by Rudolphi,[6] who found the temperature of formation to lie between 1800 and 1819° C., that is, about 200° higher than Rothmund's value. The temperature measurements were made by an optical method, as were also Rothmund's. Finally, Lampen,[7] by a method similar to the above, using a Wanner pyrometer for temperature measurements, found 1725° C. for the temperature of formation. It seemed evident, from the poor agreement of these results, all obtained by the same method, that some other method would have to be used in which the pressure of the carbon monoxide could also be measured, as these differences might be due simply to different values of this quantity. It was the object of the following investigation to make these measurements.

2. Method and Results.

The method decided on was to heat the charge in a vacuum furnace connected with a mercury manometer and to measure the temperature of the charge and pressure of the carbon monoxide when equilibrium is reached. A small Arsem [8] vacuum furnace, made by the General Electric Company, was the apparatus used. It consists of a cylindrical bronze casting 24 centimeters in inside diameter and 39 centimeters in length. Parallel to the axis in the center of the casting and fastened to the lid, is a graphite helix, 27 centimeters in length, 5.1 in outside diameter and 0.5 in thickness of wall. The helix is clamped at each end by water-cooled electrodes. The lid is fastened to the casting with a number of cap-screws and a lead washer. The whole furnace is immersed in water with the exception of a tower projecting from the center

[5] Rothmund erroneously assumes the pressure of the carbon monoxide to be 1/5 atmosphere, probably because this is the partial pressure of oxygen in the atmosphere. Taking into consideration that every mole of oxygen produces two of carbon monoxide, 1/3 atmosphere is the result obtained.

[6] Zeitschr. f. anorg. Chem. 1907, **54**, 170.

[7] Jour. Am. Chem. Soc., 1906, **28**, 864.

[8] Trans. Am. Electrochem. Soc., 1906, **9**, 163.

of the lid containing a mica window, making it possible to see the hot material held in the center of the spiral. The support for the crucible is a graphite rod held by the lower electrode, but insulated by lava rings. The lid also contains a pipe by which the furnace may be exhausted. A Geryk oil pump was used for obtaining the vacuum. The pressure could be read by a wooden scale divided in millimeters on a mercury gauge completely evacuated and sealed off at one end, thus

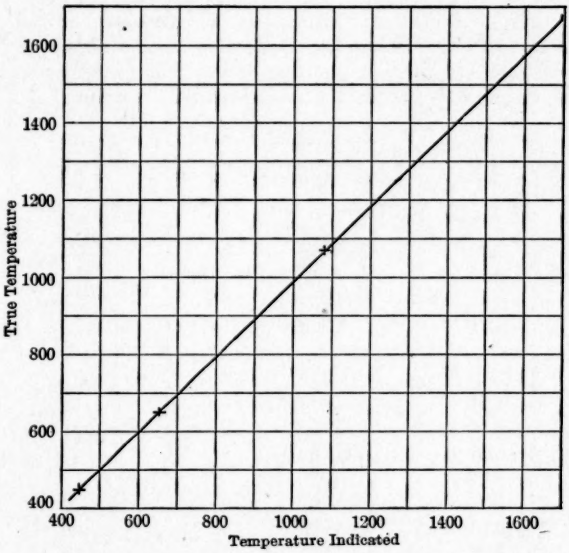

FIGURE 1. Calibration of Thermoelectric Junction.

making a siphon barometer. The temperature of the gas contained in the furnace is not constant, but all that determines the equilibrium besides the pressure is the temperature of the solid substances and of the gas in contact with it. Of course the pressure must be constant throughout the furnace.

In the first experiments the temperature was measured by a Wanner pyrometer, which rendered it necessary to replace the mica window by one of glass clamped between rubber and sealed up with paraffin. In calibrating the pyrometer a similar piece of glass was placed between the amylacetate standard and the instrument. The Wanner was found

TABLE I.

CALIBRATION OF THERMOELECTRIC JUNCTION.

True Temperature.		Temperature read directly from scale.
Melting point of Gold . .	1065° C.	1075° C.
Melting point of Aluminum	655° C.	650° C.
Boiling Sulphur	445° C.	440° C.

to be unreliable, however, apparently due to inconstancy in the amyl-acetate standard.[9] The furnace was therefore calibrated by means of a platinum platinum-rhodium junction, that is, the temperature of the crucible was measured while the power was held constant. The tem-

TABLE II.

CALIBRATION OF FURNACE.

Kilowatts.	Temperature by thermo-electric junction.	Remarks.
3.60	968°	
7.03	1185°	
8.98	1325°	1st spiral
9.71	1368°	
3.12	925°	
4.99	1062°	
7.10	1180°	2d spiral
8.03	1225°	
9.00	1262°	
9.81	1325°	2d spiral
7.68	1180°	repeated on
6.15	1100°	following day

perature was then subsequently determined by measuring the power applied. Heating was furnished by an alternating current with a frequency of sixty cycles per second. This was taken from a transformer-switchboard so arranged that the voltage could be varied in steps of about twelve volts. For the finer regulation a carbon plate rheostat, in which current regulation could be obtained by varying the compres-

[9] The temperatures measured in the former article on this subject are accordingly from 100° to 150° too low, but the general conclusions there reached are not affected.

sion on the plates was found satisfactory. The terminals were copper boxes filled with water.

Figure 1 gives the calibration of the junction. The galvanometer

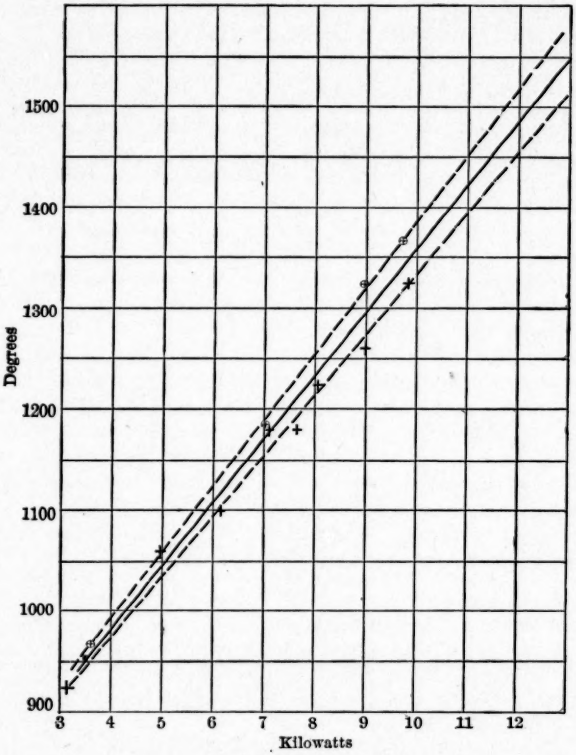

FIGURE 2. Calibration of Furnace.

was a Siemens and Halske instrument made for this special purpose, but which did not read as high as the melting point of platinum.

In Table II and Figure 2 the calibration of the furnace is given. The power was obtained from voltmeter and ammeter readings. The ammeter scale read to five amperes and was connected to a current transformer with a ratio of 60 to 1. This instrument was not calibrated.

Two voltmeters with scales from 0–65 and 40 to 160 were used. These were calibrated so as to make them comparable with each other. The alternating current instruments were of the Thomson type made by the General Electric Company.

In calibrating the furnace the wires of the pyrometer were protected by fused silica tubes which extended up into the tower in the lid of the furnace. The tubes were covered at the junction by a short graphite tube. This projected through a hole in the cap of the crucible containing the charge and rested in the charge. The bare wires were brought out of the furnace at the top of the tower between rubber washers; the furnace was then evacuated and the calibration taken.

TABLE III.

VARIATION OF TEMPERATURE IN CRUCIBLE.

Distance of junction from bottom of crucible.	Temperature.
0.0 cm.	1220°
0.6	1220°
1.8	1225°
3.3	1225°
4.0	1220°
4.4	1215°
4.8	1205°

The power was 8.36 kilowatts.

The carbon shield surrounding the spiral was not used in these experiments on account of the fact that carbon absorbs a large amount of gas which is not easily removed. It will be evident from the method of experimenting described below that its use would not be permissible.

In the figure a circle is put around those points taken with the first spiral. It is evident from this figure that this method of obtaining the temperature is not as accurate as the Wanner pyrometer would be were it in good condition.

It will be seen that there is no regular difference in the calibration of the two spirals, except that all the points of the first coil lie on the upper dotted line, while some of the points for the second coil lie on the upper as well as the lower. This is probably due to the fact that the second spiral was calibrated more than once. It was thought best under the circumstances to draw the solid line midway between the two extremes and take this for estimating the temperature.

A further test was made to see how constant the temperature was throughout the length of the crucible. For this purpose the junction,

protected by silica tubes, was lowered through the window in the tower into the crucible and the furnace heated without pumping out the air. There was no lid on the crucible in this experiment. The results are given in Table III.

It is seen that without the lid and with no charge in the crucible the temperature is quite constant, which would be improved, if anything, when the charge is in the crucible and the lid in position.

The carbide used in the following experiments was made from Merk's lime and Acheson graphite powder in the form of turnings from graphite electrodes. Carbide was made by heating a mixture of the two in an arc furnace consisting of a graphite electrode and graphite crucible. By the loss in weight method [10] it analyzed 78 per cent pure. The impurities must have been carbon and lime which were not harmful for these experiments.

The first experiments were carried out at from 1700° to 2000°, but no consistent results could be obtained. After a run at these temperatures it was found that the walls of the furnace were always lined with a white powder, whether lime and carbon were heated alone or when carbide was in an atmosphere of carbon monoxide. It was found when carbide was heated in carbon monoxide to about 1800° only graphite was left in the crucible and the white powder was formed on the walls. When carbide was heated alone in a vacuum the walls of the furnace were lined with a thin sheet of calcium, which easily peeled off and took fire when brought in contact with moisture. Graphite was left behind in the crucible. These two facts taken together show that calcium reduces carbon monoxide according to the equation :

$$Ca + CO = CaO + C.$$

Therefore, if carbide is to be produced, it must either be below the temperature where it breaks up into its elements, or the velocity of the reaction

$$CaO + 3\ C = CaC_2 + CO$$

must be greater than the velocity of the preceding reaction. The latter is evidently the state of affairs in the manufacture of carbide, but equilibrium measurements could hardly be made under this condition.

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[10] Lunge, Chemische–technische Untersuchungs Methoden, 5te Auflage, Band II, 711. The drying tube contained a layer of P_2O_5 besides one of $Ca\ Cl_2$, which the escaping gas had to pass first.

From a number of experiments, which it is not necessary to reproduce here, it seemed that 1500° C. was about the highest temperature at which equilibrium could be measured. This conclusion was based on the quantity of white powder found on the walls of the furnace after runs at different temperatures. Some further experiments at about this temperature showed that it would be impossible to differentiate between the pressure of carbon monoxide and occluded gases that came out of the carbon spiral and the charge on heating in a vacuum. It was therefore decided to heat the charge in some indifferent gas, which could be drawn off and analyzed for the amount of carbon monoxide present. Hydrogen was of course the only gas available. Nitrogen could not be used on account of the fact that it is absorbed by calcium carbide forming calcium-cyanamide. Hydrogen would have no action on carbide,[11] but it does enter into an equilibrium with carbon monoxide according to the reaction

$$H_2O + C \rightleftarrows H_2 + CO$$

which is the reaction of water-gas formation. If an appreciable quantity of water were produced from hydrogen and carbon monoxide this would react with the carbide and form acetylene and in analyzing for carbon monoxide by absorption in cuprous chloride solution, acetylene would be mistaken for the former. It can be shown, however, that the quantity of water vapor formed is too small to have any effect. The free energy of this reaction is given by the equation[12]

$$\Delta F = -27950 + 31.76\,T + 4.58\,T \log \frac{p_{H_2O}}{p_{CO}\,p_{H_2}}$$

where T is the absolute temperature and the p's are partial pressures. At equilibrium $\Delta F = 0$, therefore placing the right-hand side of the equation equal to zero, and substituting for T its value 1773° absolute, we find that for 1500° C.

$$\frac{p_{H_2O}}{p_{CO}\,p_{H_2}} = 0.000324.$$

If p_{H_2} equals about 90 centimeters of mercury as it does in the following experiments,

$$\frac{p_{H_2O}}{p_{CO}} = 0.0029$$

[11] Moisson, "The Electric Furnace," p. 211.

[12] Bodländer, Zeitschr. f. Elektrochem. 1902, **8**, 833.

or $p_{H_2O} = 0.003\ p_{CO}$, which is a negligible quantity. The temperature of the gas, however, is not all at 1500°, but falls off to the temperature of the water cooled walls of the furnace. At 1000° C. $p_{H_2O} = .063\ p_{CO}$ which is still a relatively small amount. What actually happens is that at the higher temperatures where the velocity of the reaction is great, the equilibrium varies uniformly with the temperature, but as the gas reaches the cooler portions of the furnace, due to convection currents, it suddenly becomes chilled to a point where the reaction practically stops, leaving the concentrations at values corresponding to the higher temperatures.

Experiment 1.

The charge consisted of lime, carbon, and calcium carbide mixed together. A loosely fitting lid with a quarter-inch hole in the center covered the crucible. The mixture was placed in the furnace, the furnace was evacuated, and the charge heated to 1000° for an hour to drive off gases that invariably come off on the first heating, and particularly to get rid of any water contained as hydrate of calcium. If this were not done water would come off during the run and react with the carbide present. The furnace was then evacuated to a pressure of 0.05 centimeters of mercury and carbon monoxide let in to 1.25 centimeters. This was generated from strong sulphuric acid and potassium ferrocyanide and was washed with two drying towers of soda lime and a phosphorous pentoxide tube. Hydrogen was then admitted to a final pressure of 63.6 centimeters. This was generated from hydrochloric acid and zinc and was purified by two bottles of permanganate, a hot copper gauze, two towers of soda lime, and a phosphorus pentoxide tube. The furnace was filled with hydrogen in three quarters of an hour. The volume of the furnace, after allowing for the solids present during a run was 19.9 liters. The run began at 9.45 A. M. and lasted till 4.00 P. M. The power was held constant at 12.0 kilowatts corresponding to 1485° C. The following table gives the analysis for carbon monoxide, made by drawing off 100 cubic centimeters into a Hempel burette and absorbing with acid cuprous chloride solution.

Time.		Per cent Carbon Monoxide.
9.45 A. M.	Sample taken as furnace warmed up.	1.05
1.42 P. M.		Less than 0.1

It was evident from this result that the quantity of gas corresponding to equilibrium at this temperature could not be analyzed by a Hempel

apparatus. The experiment was continued till 4.00 P. M. to make sure equilibrium had been reached. The method used to determine the small quantity of carbon monoxide present in this and all the following experiments was to draw about half the gas in the furnace through two Liebig bulbs sealed together and filled with cuprous chloride solution. These were tilted at an angle so the gas bubbled through the liquid on leaving each of the five spheres of which a Liebig bulb is composed. The gas then passed a column seven centimeters long of soda lime and another similar one of phosphorous pentoxide. This whole apparatus was made entirely of glass closed by two glass stopcocks. The bulbs, in which the air was displaced by hydrogen, were hung in the balance case by a platinum wire the day before the final weight was taken. The air in the balance case was dried by two beakers of sulphuric acid and the temperature was read from a thermometer in the case. The volume of the bulbs was determined by the bottle method for specific gravity, in which a large desiccator took the place of the bottle. This was necessary in order to be able to reduce the weighings to vacuo. From the total weight in grams of carbon monoxide absorbed the number of moles is formed by dividing by 28, the molecular weight of the gas. This, however, gives only a fraction of the total amount in the furnace. The total amount is calculated as follows. If n_1 = the total number of moles in the furnace before any gas is removed, n_2 the number after a certain amount had been drawn off through the absorption bulbs, p_1 = the pressure in the furnace when the absorption began and p_2 the pressure at the end, then

$$p_1 v = n_1 R T_1$$
$$p_2 v = n_2 R T_2$$

where v equals the volume of the furnace. The temperatures were equal to those of the water surrounding the furnace and were made equal to each other at the start and finish.

Therefore $$\frac{n_1}{n_2} = \frac{p_1}{p_2}$$

also $$n_1 - n_2 = m$$

if m = the number of moles absorbed.

Solving $$n_1 = \frac{m}{1 - \frac{p_2}{p_1}}$$

If p_3 = the total pressure during the run, which is greater than p on account of the higher temperature, the pressure in millimeters of carbon monoxide is computed by the formula

$$p = \frac{m \times .0821 \times T \times 760 \times p_3}{19.9 \times p_1}$$

in which T is the absolute temperature of the gas in the furnace at the beginning and at the end of the absorption.

At the end of the absorption the pressure of hydrogen in the absorption bulbs was only about half an atmosphere, consequently enough hydrogen had to be let in to bring the pressure to one atmosphere, after which the bulbs were again hung in the balance case and weighed the following day. The variation due to temperature and pressure change in the weight of hydrogen filling the bulbs was negligible. All weighings given in the following are reduced to vacuo. The data thus obtained after the above run were the following :

Initial weight bulbs	175.3392 grams
Final " "	175.3482 "
Gain in weight	0.0090 "

The time taken for absorbing the gas was 6 hrs.

$p_1 = 68.5$ cm. of mercury
$p_2 = 38.6$ " " "
$p_3 = 89.0$ " " "

$$\text{whence } p_{CO} = \frac{.00074 \times .0821 \times 285 \times 760 \times 89}{19.9 \times 68.5}$$

$$= 0.86 \text{ mm. of mercury.}$$

On opening the furnace white powder was found on the lid.

Experiment 2.

The same charge as used in Experiment 1 was ground up and replaced in the crucible. Part was tested with water and gave off acetylene vigorously. It was heated for an hour to 1000° and evacuated to a pressure of 0.05 centimeter of mercury. No carbon monoxide was admitted. Hydrogen was let in to 6.72 centimeters in 1 hr. 40 min.

Duration of run : 6 hrs.	
Power : 11.7 K. W.	
Temperature : 1465° C.	
Initial weight bulbs	182.5989 grams
Final " "	182.6061 "
Gain	0.0072 "

Time taken for absorption 4½ hours.

$$p_1 = 67.2 \text{ cm. of mercury}$$
$$p_2 = 38.1 \text{ " " "}$$
$$p_3 = 91.8 \text{ " " "}$$

$$\therefore p_{CO} = \frac{.000589 \times .0821 \times 288 \times 760 \times 91.8}{19.9 \times 67.2} = 0.73 \text{ mm.}$$

On opening the furnace somewhat more white powder found on the walls than in Experiment 1.

This experiment was carried out with the idea of approaching the equilibrium from the side which generates carbon monoxide. To decide whether this had been done in the above experiment it was necessary to see whether the bulbs would gain no weight if the furnace were filled with hydrogen and part then drawn through the bulbs. The following blank experiment was therefore carried out. The furnace was evacuated to a pressure of 0.15 centimeter of mercury, hydrogen was let in to 1 centimeter and again evacuated to 0.15. This operation was repeated and hydrogen then let in to 67.6 centimeters. The final filling took 1 hr. 40 min.

The gas then drawn through the weighed bulbs for 3 hrs. 45 min.

$$p_1 = 67.1 \text{ cm. of mercury}$$
$$p_2 = 38.1 \text{ " " "}$$

Initial weight reduced	182.606 grams
Final " "	182.627 "
Gain	0.021 "

If the whole amount of gas could have been drawn through the gain in weight would have been 0.049 gram. This gain in weight must have been due to oxygen, which might not have been removed or which might have gotten in while filling the furnace. This would have been converted to carbon monoxide by the hot carbon spiral giving too high a pressure for equilibrium. Equilibrium in Experiment 2 was therefore

approached from the same side as in Experiment 1. This remark holds good for all the following experiments.

Experiment 3.

As the previous experiments agreed fairly well, it was thought desirable to try a lower temperature, to make sure that the gain in weight of the absorption bulbs was really due to carbon monoxide and not to some impurity in the hydrogen.

The charge consisted of fresh carbide, lime and carbon. The furnace was evacuated to 0.15 centimeter and was heated to 1000° till the occluded gases coming off gave a pressure of 6 centimeters, which required about ten minutes. It was then evacuated to 0.15 centimeter with the furnace still at 1000°. Hydrogen was let in to 2.4 centimeters and evacuated to 0.15. The furnace was then cooled and filled with hydrogen to a pressure of 67.0 in 1 hr. 40 min.

Power : 8.24 K. W.
Temperature : 1250°
Duration of run : 6 hrs.

The solution of cuprous chloride had been used in a previous experiment.

Initial weight of absorption bulbs	183.6340	grams
Final " " " "	183.6372	"
Gain	0.0032	"

$p_1 = 67.2$ cm. of mercury
$p_2 = 34.8$ " "
$p_3 = 90.4$ " "

$$\therefore p_{CO} = \frac{0.000248 \times .0821 \times 286 \times 760 \times 90.4}{19.9 \times 67.2} = 0.30 \text{ mm.}$$

Experiment 4.

The charge was the same material as in the previous experiment with some lime and carbon added and mixed up with the rest.

The furnace was evacuated to a pressure of 0.2 centimeter and heated to 900° for two hours. It was then evacuated to 0.15 centimeter, hydrogen was admitted to 2.4 and again evacuated to 0.15. It was finally filled with hydrogen to 67.3 centimeters in 1 hr. 40 min.

Power : 8.8 K. W.
Temperature : 1270°
Duration of run : 7 hrs. 10 min.

The absorption bulbs were refilled.

Initial weight	182.9303	grams
Final "	182.9316	"
Gain	0.0013	"

$p_1 = 66.8$ cm. of mercury
$p_2 = 37.2$ " " "
$p_3 = 90.3$ " " "

$$\therefore p_{CO} = \frac{0.000103 \times .0821 \times 285 \times 760 \times 90.3}{19.9 \times 66.8} = 0.13 \text{ mm.}$$

Experiment 5.

The object of the following experiment was to see if measurements might not be carried out at a somewhat higher temperature where the pressure would be greater and the determination therefore more accurate.

The charge was the same carbide used in experiment 4 to which about one half as much lime and carbon, previously heated to redness, was added. The furnace was then evacuated to 0.2 centimeter and heated to 900° for 1¼ hours. It was then evacuated to 0.2 centimeter and hydrogen let in to 2.3; again evacuated to 0.12 centimeter and filled with hydrogen to 67.7.

The charge was then heated 7 hours with 10.0 kilowatts, corresponding to 1370°. This must have established equilibrium at this temperature. The power was then raised to 12.6 kilowatts corresponding to 1525° for 4¼ hours.

The cuprous chloride was the same used in Experiment 4.

Initial weight	182.9243	grams
Final "	182.9277	"
Gain	0.0034	"

Time taken for absorption 3 hrs.

$p_1 = 66.3$ cm. of mercury
$p_2 = 37.7$ " " "
$p_3 = 90.0$ " " "

$$\therefore p_{CO} = \frac{.000280 \times .0821 \times 285 \times 760 \times 90.0}{19.9 \times 663} = 0.34 \text{ mm.}$$

On opening the furnace a larger amount of powder than any other experiments here given was found on the walls. This, taken in connection with the small pressure found and the experiments referred to in the Introduction seem to indicate that at this temperature the carbon monoxide was removed by calcium coming from the decomposition of carbide.

It is true that this equilibrium was really approached from the side of too little carbon monoxide, but as the velocity of the reaction is the same in both directions at equilibrium, this cannot account for the low pressure of carbon monoxide.

Experiment 6.

The hydrogen used in the following experiments was generated electrolytically on platinum electrodes dipping into sulphuric acid of 1.2 specific gravity. The cathodes were contained in a porous cup closed at the top by a cork stopper covered with paraffin, through which projected glass tubes, into which the electrodes were sealed. There was also a tube through which hydrogen could escape. The porous cup stood in a small battery jar. The hydrogen tube was connected to a mercury manometer so that the pressure in the cathode compartment could be kept from 0.1 to 1.0 centimeter above the atmosphere, thereby preventing air from leaking in. In Experiment 6 only one such electrolytic cell was used, but for the last two experiments another cell was connected in series with the first, thus requiring only half the time for filling the furnace. The hydrogen first passed through a soda lime tube, then the hot copper gauze used in the previous experiments, then two soda lime towers and phosphorous pentoxide tube. Hydrogen was passed over the hot copper for at least half an hour before any was let into the furnace, in order to sweep out the air in the tube. The object in using electrolytic hydrogen was to show that the above gains in weight were not due to impurities in the hydrogen generated from zinc and hydrochloric acid.

The carbon monoxide used in the following experiments was generated by allowing formic acid to drop from a separatory funnel into concentrated sulphuric acid.

In order to see if all the carbon monoxide was absorbed by the two Liebig bulbs containing cuprous chloride in the following experiments a second absorbing apparatus similar to the above was used with one Liebig bulb in place of two. This was filled with a 3 per cent solution

of neutral gold chloride. This has been found to oxidize carbon monoxide to dioxide without affecting hydrogen.[13] Gold chloride in an excess of potassium hydrate is even more sensitive to carbon monoxide, but it was found that hydrogen reduced the gold in the alkaline solution to a black powder if left in contact with the solution over night.

The charge consisted of about equal portions of powdered carbide and a mixture of lime and carbon. It had been used in a previous run.

The cuprous chloride in the Liebig bulbs had been used in the three previous experiments, but as a little was tested with water and gave a heavy white precipitate it was not thought necessary to change the solution.

The furnace was evacuated to a pressure of 0.28 centimeter and hydrogen was let in to 1.0 centimeter; then evacuated to 0.1 and carbon monoxide let in to 0.3 centimeter. Hydrogen was then admitted to 67.3 centimeters requiring three hours with a current of about 14 amperes.

Duration of run: $6\frac{1}{2}$ hours.
Power: 11.8 K. W.
Temperature: 1475°

Initial weight cuprous chloride bulbs	173.1312 grams
Final " " " "	173.1383 "
Gain	0.0073 "
Initial weight gold chloride bulb	116.8119 grams
Final " " " "	116.8158 "
Gain	0.0036 "
Total gain	0.0110 "

The gain in the gold chloride bulbs was relatively large, probably on account of the cuprous chloride having taken so much carbon monoxide into solution that it was not so good an absorber as when fresh.

$$p_1 = 65.7 \text{ cm. of mercury}$$
$$p_2 = 34.5 \text{ " "}$$
$$p_3 = 92.0 \text{ " "}$$

$$\therefore p_{CO} = \frac{0.000703 \times 0.0821 \times 287 \times 760 \times 92}{19.9 \times 65.7} = 0.88 \text{ mm.}$$

[13] Phillips, Am. Chem. Journ. 1894, **16**, 273.

Experiment 7.

The charge consisted of powdered carbide with some coarser pieces on top. It was heated in the furnace at 1050° for an hour and a quarter and evacuated to 0.1 centimeter. Hydrogen was then let in to a pressure of 1.6 centimeters, the furnace was evacuated to 0.10 and carbon monoxide let in to 0.25 centimeter. Finally hydrogen was let in to 68.3 centimeters requiring one hour and a half with 14 amperes.

Duration of run: 6 hours
Power: 11.8 K. W.
Temperature: 1475°

The cuprous chloride bulbs were refilled, but not the gold chloride.

Initial weight cuprous chloride bulbs	173.7646 grams
Final " " " "	173.7695 "
Gain	0.0049 "

Initial weight gold chloride bulb	116.8121 grams
Final " " " "	116.8126 "
Gain	0.0005 "
Total gain	0.0054 "

Time required for absorption, 3 hours.

$$\therefore p_{CO} = \frac{0.00065 \times 0.0821 \times 291 \times 760 \times 95}{19.9 \times 69.3} = 0.81 \text{ mm.}$$

Experiment 8.

The charge was the same material as used in Experiment 7.

The furnace was evacuated and heated for an hour and fifty minutes at 1050°. It was then evacuated to a pressure of 0.12 centimeter and hydrogen let in to 2.0, again evacuated to 0.15 and carbon monoxide let in to 0.28 centimeter. Hydrogen was then admitted to 77.6 centimeters requiring an hour and a quarter.

Duration of run: 6 hours, 10 minutes.
Power: 11.4 K. W.
Temperature: 1445° C.
The cuprous chloride bulbs were refilled.

Initial weight of cuprous chloride bulbs	167.4274 grams
Final " " " " "	167.4312 "
	0.0038 "

The tube previously used for gold chloride was filled with cuprous chloride.

Initial weight of second cuprous chloride tube		119.3358 grams
Final " " " " " "		119.3363 "
Gain		0.0005 "
Total gain	0.0043	

$p_1 = 67.1$ cm of mercury
$p_2 = 37.7$ " "
$p_3 = 92.7$ " "

The time taken for absorption was $3\frac{1}{4}$ hours.

$$\therefore p_{CO} = \frac{.000350 \times 0.0821 \times 287 \times 760 \times 92.7}{19.9 \times 67.1} = 0.44 \text{ mm.}$$

3. Discussion of Results.

For convenience the results obtained above are collected in the following table.

TABLE IV.

No. of Exp.	Duration in Hours.	Kilowatts.	Temp. Centigrade.	Gain in Weight of 1st Bulb.	Gain in Weight of 2d Bulb.	Time taken for Absorption in Hours.	Initial Pressure CO in mm. Hg.	Final Pressure CO in mm. Hg.
1	$6\frac{1}{2}$	12.0	1485	0.0090	. . .	6	12.5	0.86
2	6	11.7	1465	0.0072	. . .	$4\frac{1}{2}$	0.0	0.73
3	6	8.2	1250	0.0032	. . .	$3\frac{1}{2}$	0.0	0.30
4	7	8.8	1270	0.0013	. . .	$2\frac{2}{3}$	0.0	0.13
5	$4\frac{1}{2}$	12.6	1525	0.0034	. . .	3	0.0	0.34
6	$6\frac{1}{4}$	11.8	1475	0.0073	0.0036	4	2.0	0.88
7	6	11.8	1475	0.0049	0.0005	3	1.5	0.81
8	6	11.4	1445	0.0038	0.0005	$3\frac{1}{4}$	1.3	0.44

In all of these experiments, even at 1250°, there was some white powder on the walls of the furnace. Whether a slight decomposition of carbide into its elements takes place at this temperature could not be decided by this means, as the white powder may have been due to

two causes, both the decomposition of carbide and to volatilization of some impurity in the lime or carbon. The best evidence that the carbide does not break up at 1475° and does break up at 1525° is that equilibrium could be measured at the former but not at the latter temperature. Attention was called to the possibility of lime itself being somewhat volatile at 1500°, since a piece of Merk's lime heated at the melting point of platinum for an hour also produced a layer of white powder on the walls of the furnace.

As Experiments 1 and 2 were carried out at temperatures equally above and below the temperature in experiments 6 and 7, the average of these four may be taken, with the result

$$p_{CO} \text{ at } 1475°\text{C.} = 0.82 \pm .02 \text{ mm.}$$

Through these results were obtained from the same side of the equilibrium, different amounts of carbon monoxide were present at the beginning in each case, which makes the evidence that equilibrium had been reached conclusive.

From this result, the pressure obtained in Experiment 8 at a temperature 30° lower may be checked by the integrated van't Hoff equation :

$$4.57 \log_{10} \frac{p_2}{p_1} = Q \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where p_2 and p_1 and the pressures of carbon monoxide corresponding to the absolute temperatures T_1 and T_2 and Q is the heat absorbed by the reaction, when it proceeds from left to right. Q has been calculated [14] to be 121000 calories at room temperature, with a negative temperature coefficient of 3.3 calories per degree.

Therefore $$Q = 121000 - 3.3\, t,$$

where t equals centigrade degrees above room temperature, which for high temperatures may be considered as degrees above zero. For 1460° C. Q therefore equals 116000 calories. Substituting in the above equation the absolute temperatures corresponding to 1475° and 1445°, the value of $\frac{p_2}{p_1}$ comes out 1.79. The ratio between the pressures found by experiment is 1.86, which is very satisfactory agreement.

If the pressure at 1270° is calculated from that at 1475°, using the value of Q corresponding to the mean temperature 1370°, the result is

[14] Trans. Am. Electrochem. Soc., 1909, **15**, 197.

0.0093 millimeter, that is, it is below a measurable quantity. The fact that in one case 0.13 and in another 0.3 millimeters were found is due to the insufficient time allowed to absorb this very small amount of carbon monoxide.

From the value of the equilibrium pressure obtained at 1475° it is possible by the above formula to calculate the pressure at higher temperatures and see approximately what is the shape of the pressure temperature curve. The value of Q corresponding to the mean of each set of temperatures is used. 1475° is always taken as the lower temperature. The results of this computation are given in Table IV and Figure 3.

TABLE V.

PRESSURES OF CARBON MONOXIDE COMPUTED FROM THE VALUE DETERMINED AT 1475°.

Temperature Degrees Centigrade.	Equilibrium Pressure of Carbon Monoxide in Centimeters.		
	I Lower Limit.	II Mean.	III Upper Limit.
1475	0.05	0.08	0.13
1575	0.31	0.50	0.79
1675	1.54	2.53	4.00
1775	6.6	10.7	17.
1875	25.0	40.5	64.
1975	81.	133.0	210.

It is evident that the error in this curve is due practically entirely to the error in the temperature measurements, for while the value of p_1 is accurate to 2.5 per cent, the temperature is uncertain by 25°, and the value 0.82 millimeters might correspond to 1500° or 1450° as the two extremes. This would mean the true value at 1475° might be 1.3 or 0.5 millimeters as the two extremes. If now the curve be computed first with the value 1.3 in place of 0.82, and again with 0.5, the values under I and III in Table V are obtained. The values are plotted in Figure 3 in broken curves. From these curves it is seen the temperature corresponding to 1/3 of an atmosphere lies between 1800° and

1875°, with which Rudolphi's values agrees the best of all the three referred to in the Introduction.

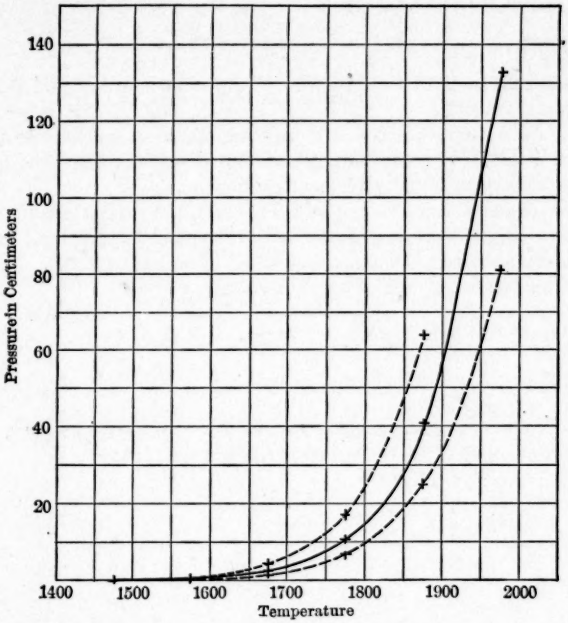

FIGURE 3. Pressure of Carbon Monoxide Computed from the Value Determined at 1475° C.

The free energy increase of the reaction taken from left to right at 1475° C. is

$$\begin{aligned} \Delta F &= RT \log \frac{760}{0.82} \\ &= 4.57 \times 1748 \log_{10} 927 \\ &= +\ 23700 \text{ calories} \end{aligned}$$

As the temperature rises ΔF decreases till at 1920°, where the equilibrium pressure equals an atmosphere, $\Delta F = 0$. Above 1920° ΔF becomes negative.

Summary of Results.

1. The equilibrium pressure of carbon monoxide in the reaction

$$CaO + 3\ C \rightleftarrows CaC_2 \times CO$$

was measured at 1475° and 1445°. The results were in good thermodynamic agreement.

2. A little below 1445° C. the pressure becomes too small to measure; a little above 1475° decomposition of calcium carbide into its elements prevents measurement of equilibrium.

3. With the aid of the heat of the reaction the vapor pressure curve at higher temperatures was computed which cannot be realized experimentally on account of the decomposition of calcium carbide.

4. The free energy increases of the reaction

$$CaO + 3\ C = CaC_2 + CO$$

at 1475° is +23700 calories.

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